TABLE 12.1 Concentrations of Reactant and Products as a Function of Time for the Reaction $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$ (at 300°C)

	Concentration (mol/L)		
Time (±1 s)	NO_2	NO	O_2
0	0.0100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033
400	0.0031	0.0069	0.0035

TABLE 12.2 Average Rate (in mol/L · s) of Decomposition of Nitrogen Dioxide as a Function of Time*

$\dfrac{\Delta[NO_2]}{\Delta t}$	Time Period (s)
4.2×10^{-5}	$0 \rightarrow 50$
2.8×10^{-5}	$50 \rightarrow 100$
2.0×10^{-5}	$100 \rightarrow 150$
1.4×10^{-5}	$150 \rightarrow 200$
1.0×10^{-5}	$200 \rightarrow 250$

*Note that the *rate* decreases with time.

Figure 12.1 Starting with a Flask of Nitrogen Dioxide at 300°C, Concentrations of Nitrogen Dioxide, Nitric Oxide, and Oxygen are Plotted versus Time

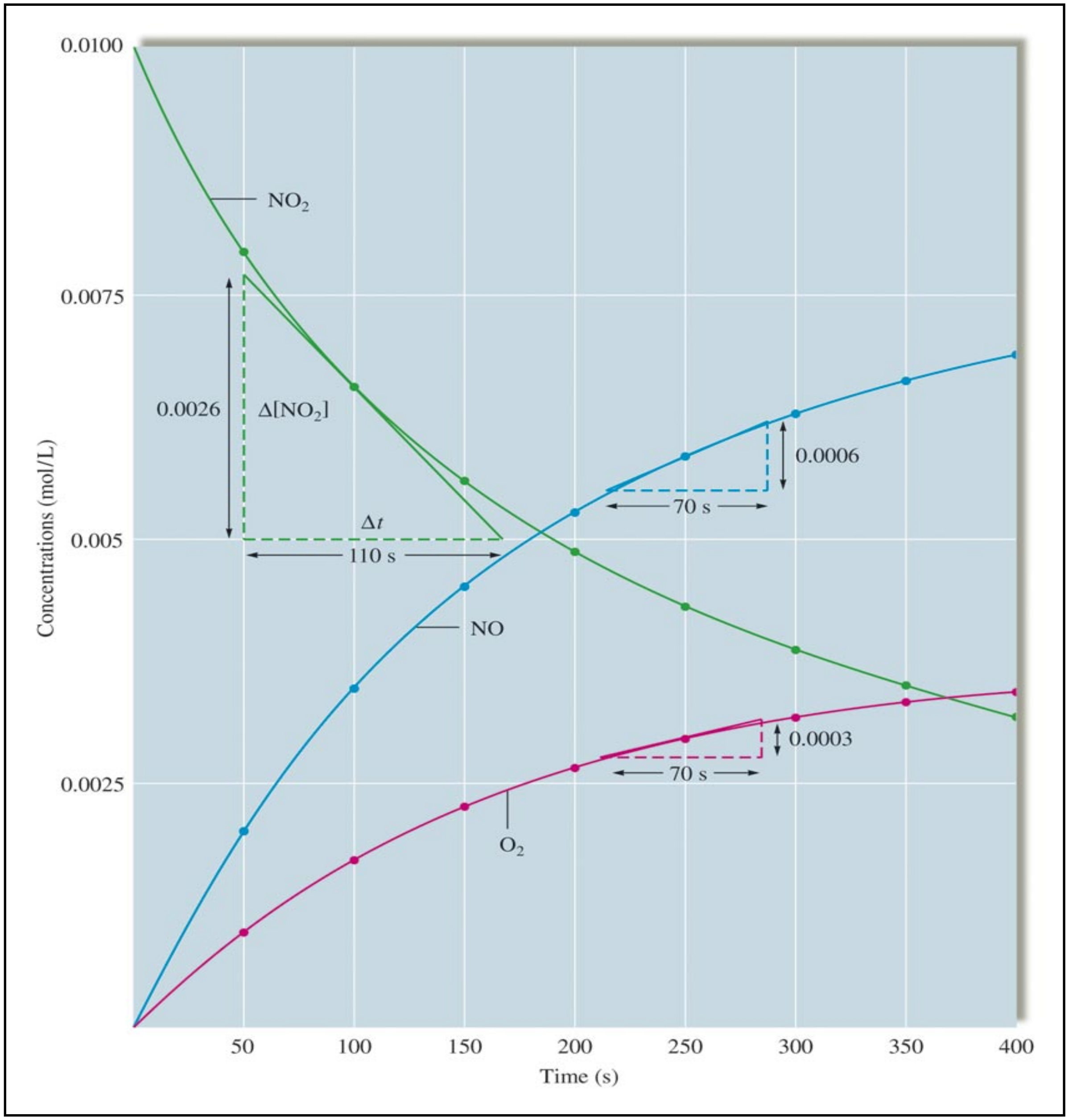


Figure 12.2 Representation of the Reaction of $2NO_2$ (g) $2NO$(g) + O_2 (g)

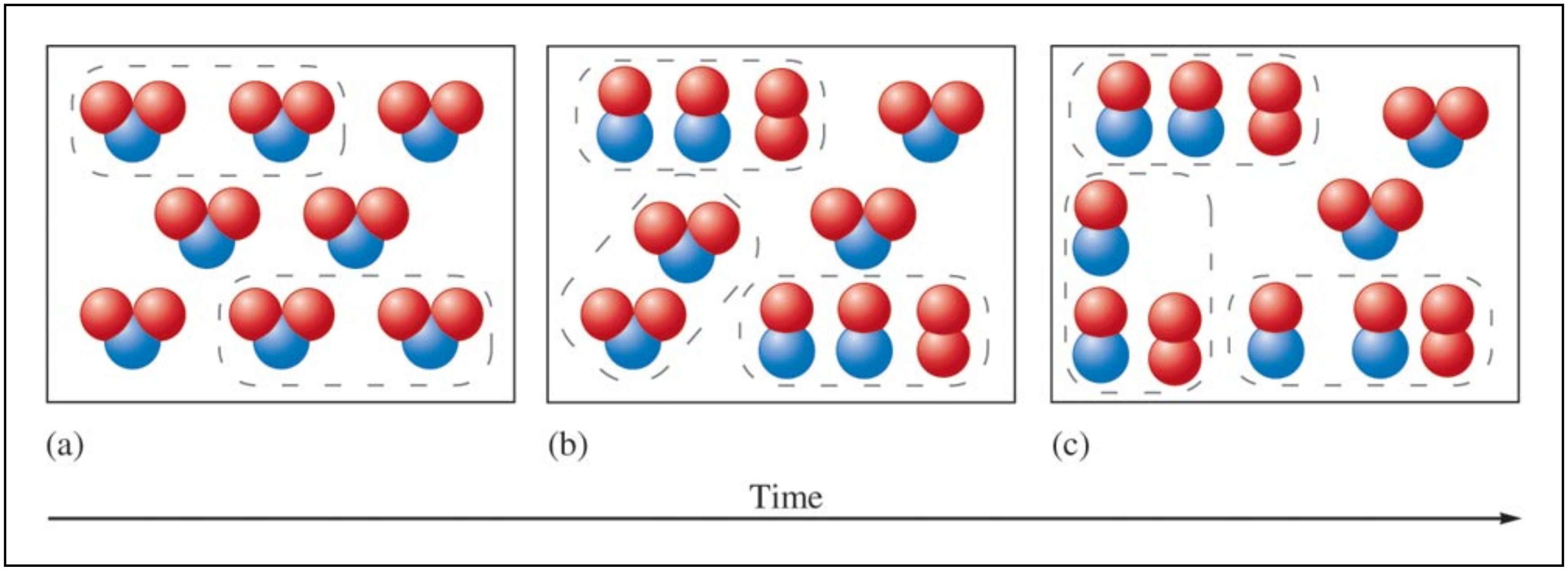


Figure 12.3 A Plot of the Concentration of N_2O_5 as a Function of Time for the Reaction

TABLE 12.3 Concentration/Time Data for the Reaction $2N_2O_5(soln) \rightarrow 4NO_2(soln) + O_2(g)$ (at 45°C)

$[N_2O_5]$ (mol/L)	Time (s)
1.00	0
0.88	200
0.78	400
0.69	600
0.61	800
0.54	1000
0.48	1200
0.43	1400
0.38	1600
0.34	1800
0.30	2000

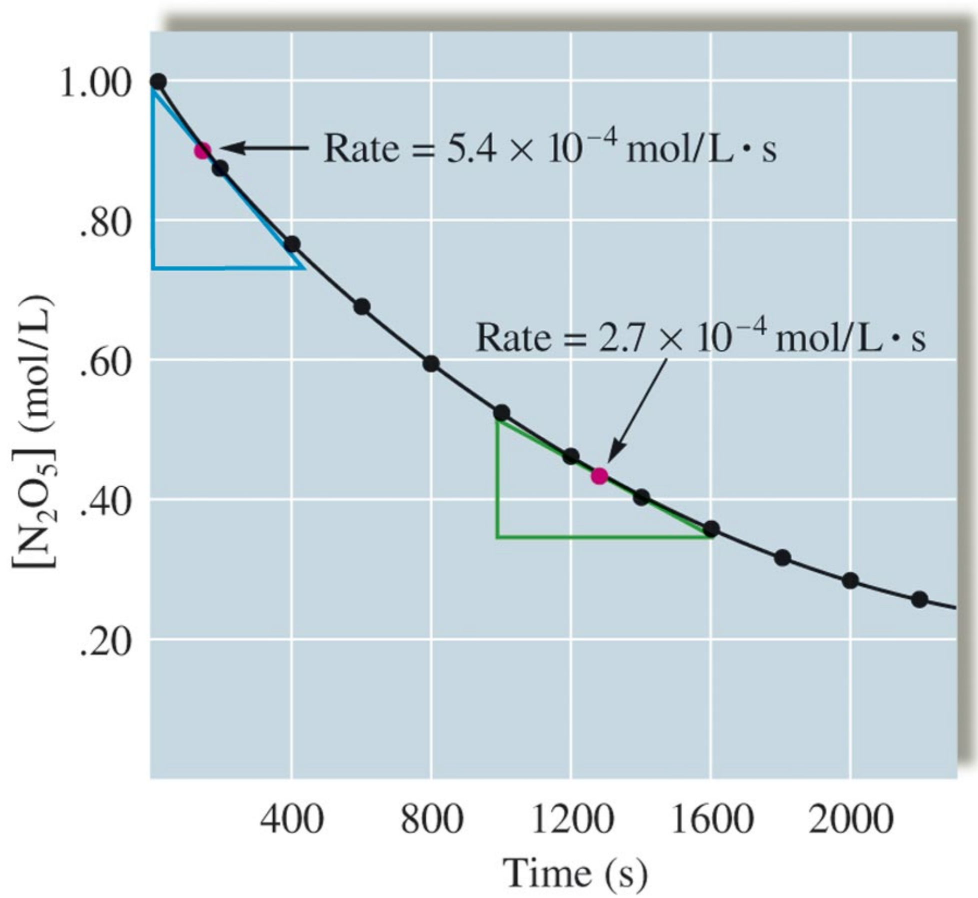


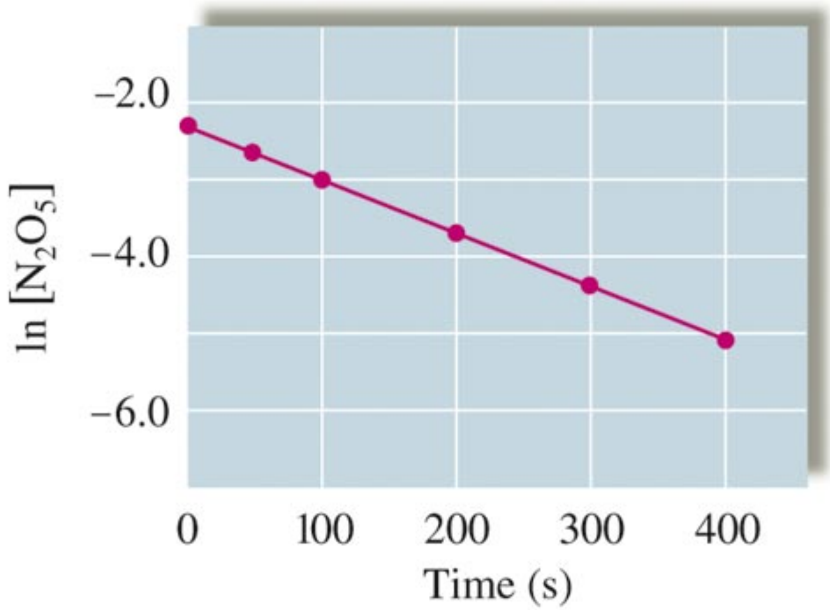
TABLE 12.4 Initial Rates from Three Experiments for the Reaction $NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l)$

Experiment	Initial Concentration of NH_4^+	Initial Concentration of NH_2^-	Initial Rate (mol/L · s)
1	0.100 *M*	0.0050 *M*	1.35×10^{-7}
2	0.100 *M*	0.010 *M*	2.70×10^{-7}
3	0.200 *M*	0.010 *M*	5.40×10^{-7}

TABLE 12.5 The Results from Four Experiments to Study the Reaction $BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(l) + 3H_2O(l)$

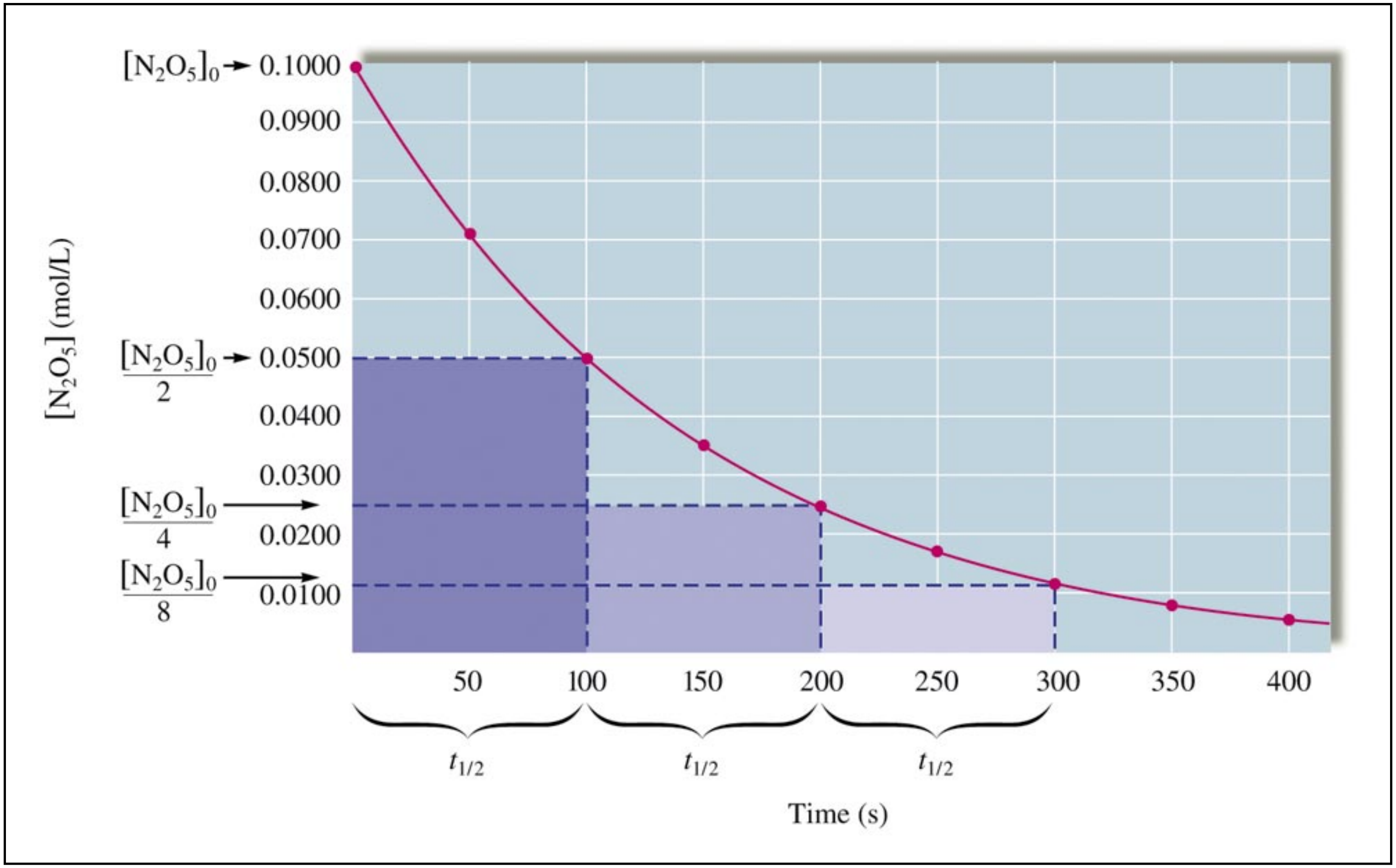
Experiment	Initial Concentration of BrO_3^- (mol/L)	Initial Concentration of Br^- (mol/L)	Initial Concentration of H^+ (mol/L)	Measured Initial Rate (mol/L · s)
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

Figure 12.4 A Plot of $\ln[N_2O_5]$ versus Time



$\ln[N_2O_5]$	Time (s)
−2.303	0
−2.649	50
−2.996	100
−3.689	200
−4.382	300
−5.075	400

Figure 12.5 A Plot of $[N_2O_5]$ versus Time for the Decomposition Reaction of N_2O_5



Problem: Consider the dimerization of butadiene.

$$2C_4H_6(g) \text{ --> } C_8H_{12}(g)$$

a. Is the reaction first or second order?

b. What is the value of the rate constant?

c. What is the half-life under the conditions of this experiment

$[C_4H_6]$ (mol/L)	Time (s)	$\ln[C_4H_6]$	$1/[C_4H_6]$
0.01000	0	-4.605	100
0.00625	1000	-5.075	160
0.00476	1800	-5.348	210
0.00370	2800	-5.599	270
0.00313	3600	-5.767	319
0.00270	4400	-5.915	370
0.00241	5200	-6.028	415
0.00208	6200	-6.175	481

Figure 12.6 (a) A Plot of ln[C_4H_6] versus t (b) A Plot of 1/[C_4H_6] versus T

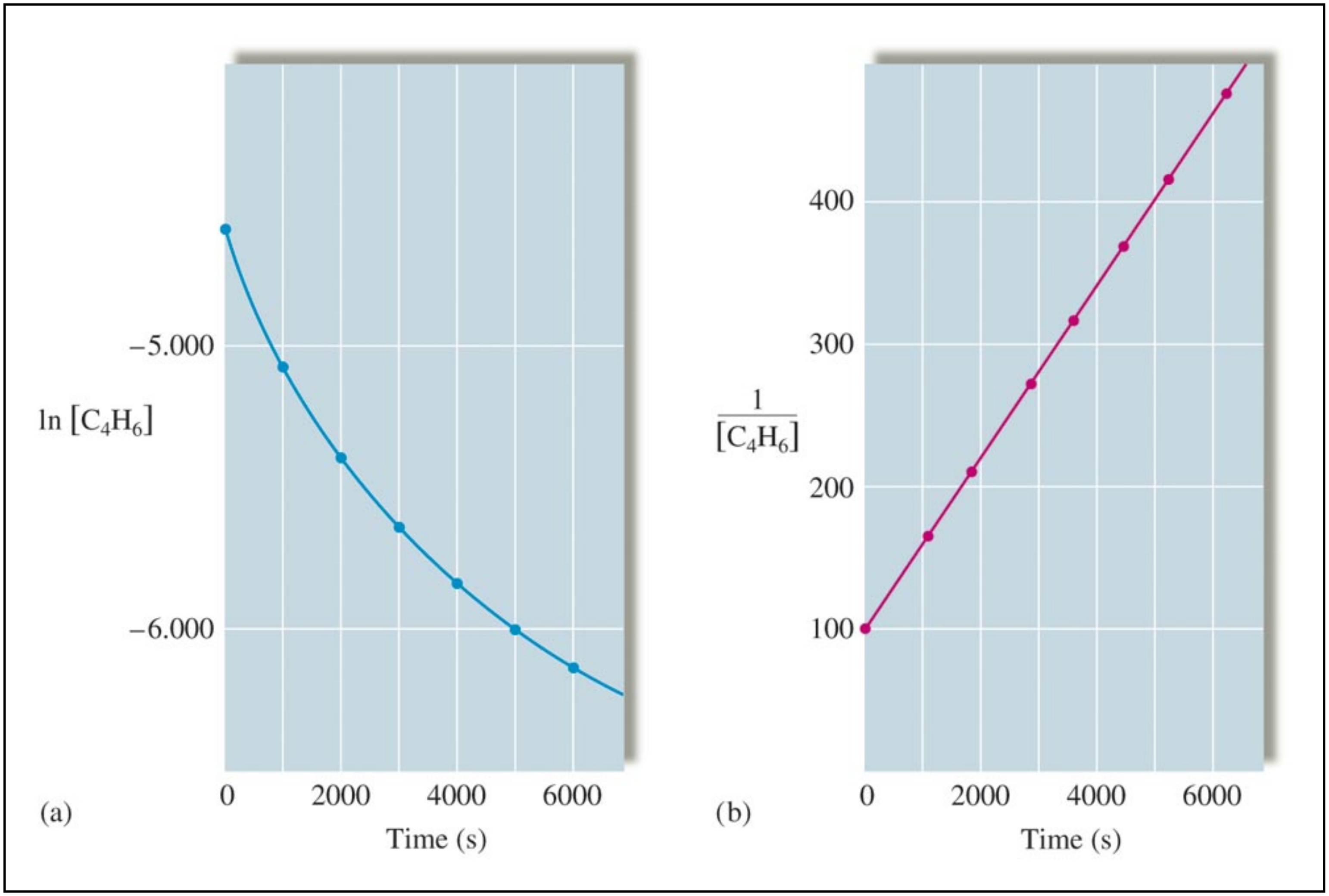


Figure 12.7
A Plot of [A] versus T for a Zero-Order Reaction

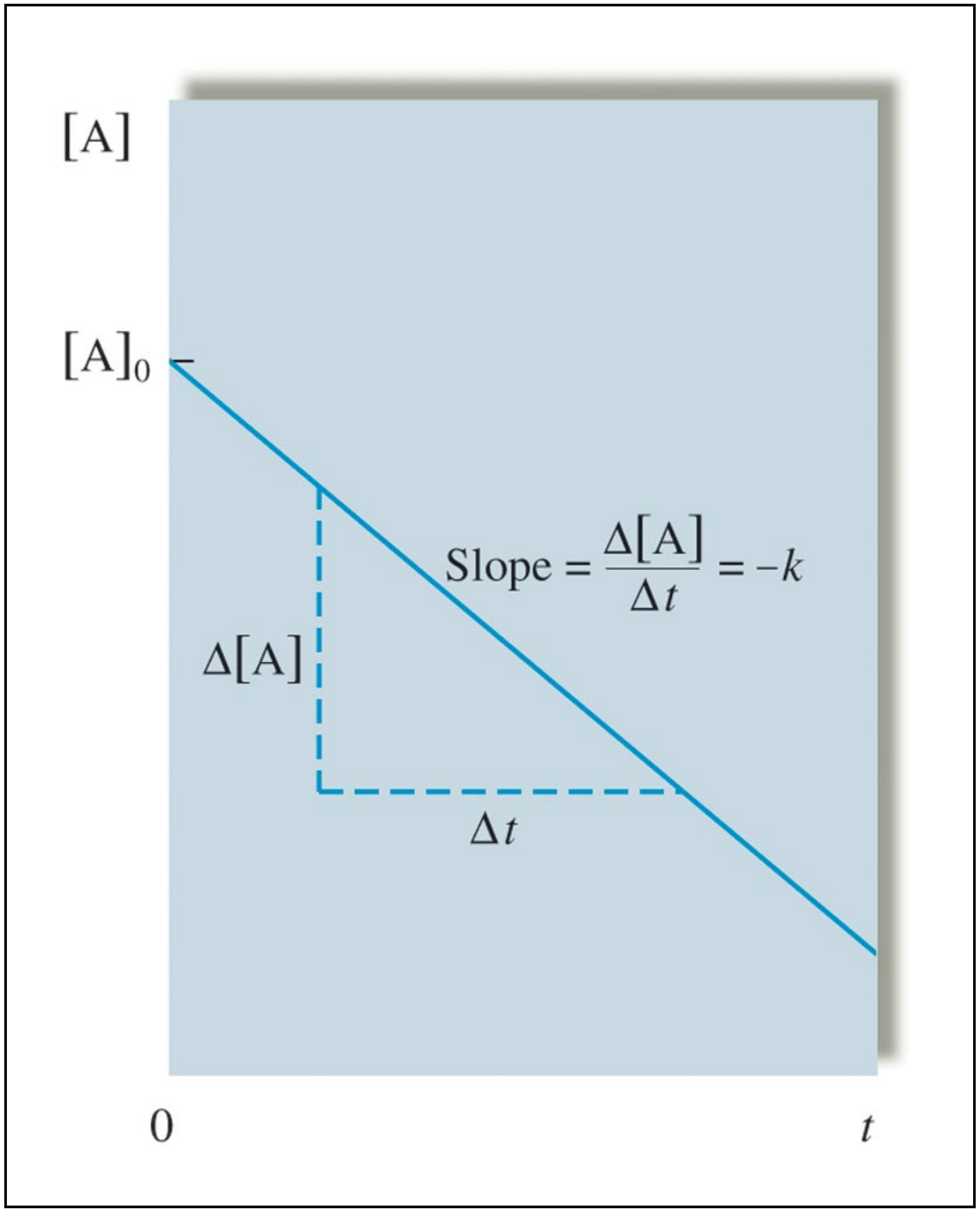


Figure 12.8 The Decomposition Reaction $2N_2O(g)$ $2N_2 + O_2$ (g) takes Place on a Platinum Surface

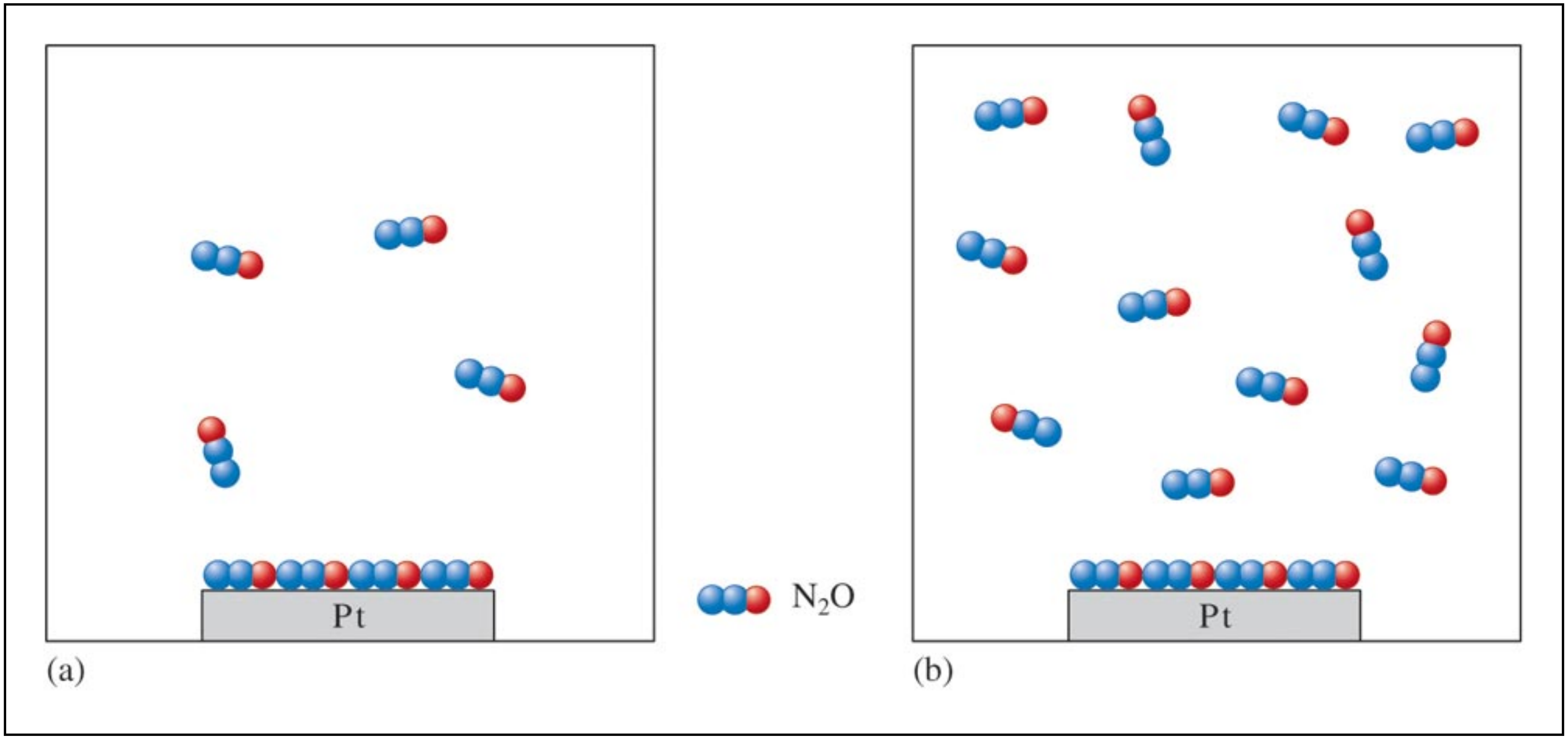


TABLE 12.6 Summary of the Kinetics for Reactions of the Type aA $\rightarrow$ Products That Are Zero, First, or Second Order in [A]

	Order		
	Zero	***First***	***Second***
Rate Law:	Rate $= k$	Rate $= k[\mathrm{A}]$	Rate $= k[\mathrm{A}]^2$
Integrated Rate Law:	$[\mathrm{A}] = -kt + [\mathrm{A}]_0$	$\ln[\mathrm{A}] = -kt + \ln[\mathrm{A}]_0$	$\frac{1}{[\mathrm{A}]} = kt + \frac{1}{[\mathrm{A}]_0}$
Plot Needed to Give a Straight Line:	$[\mathrm{A}]$ versus t	$\ln[\mathrm{A}]$ versus t	$\frac{1}{[\mathrm{A}]}$ versus t
Relationship of Rate Constant to the Slope of Straight Line:	Slope $= -k$	Slope $= -k$	Slope $= k$
Half-Life:	$t_{1/2} = \frac{[\mathrm{A}]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[\mathrm{A}]_0}$

Figure 12.9 A Molecular Representation of the Elementary Steps in the Reaction of NO_2 and CO

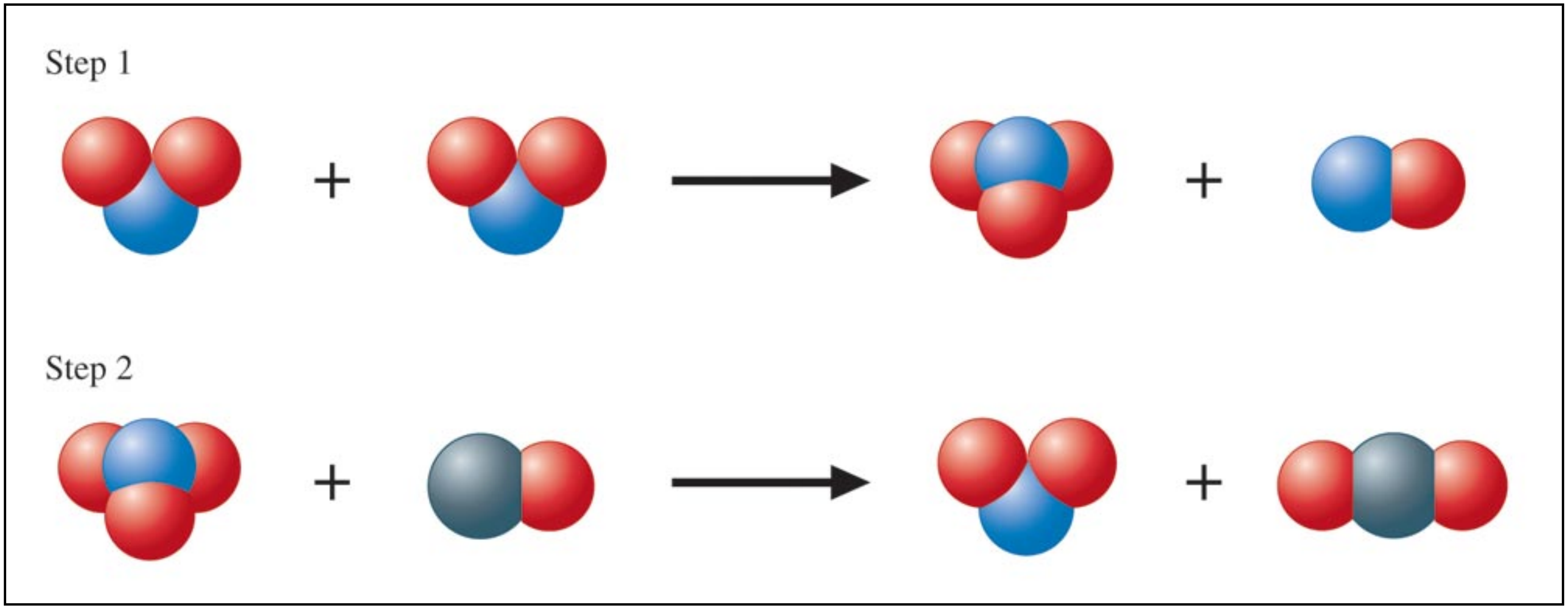


Table 12.7 Examples of Elementary Steps

TABLE 12.7 Examples of Elementary Steps

Elementary Step	Molecularity	Rate Law
$A \rightarrow$ products	*Uni*molecular	Rate $= k[A]$
$A + A \rightarrow$ products ($2A \rightarrow$ products)	*Bi*molecular	Rate $= k[A]^2$
$A + B \rightarrow$ products	*Bi*molecular	Rate $= k[A][B]$
$A + A + B \rightarrow$ products ($2A + B \rightarrow$ products)	*Ter*molecular	Rate $= k[A]^2[B]$
$A + B + C \rightarrow$ products	*Ter*molecular	Rate $= k[A][B][C]$

Step 1) $N_2H_2O_2 \rightleftharpoons N_2HO_2^- + H^+$	(fast equilibrium)
Step 2) $N_2HO_2^- \rightarrow N_2O + OH^-$	(slow)
Step 3) $H^+ + OH^- \rightarrow H_2O$	(fast)

Nitramide, $N_2H_2O_2$, decomposes slowly in aqueous solution. This decomposition is believed to occur according to the reaction mechanism above.

a. What is the rate law for each elementary step?
b. What is the rate law for the overall reaction?

Figure 12.10 A Plot Showing the Exponential Dependence of the Rate Constant on Absolute Temperature

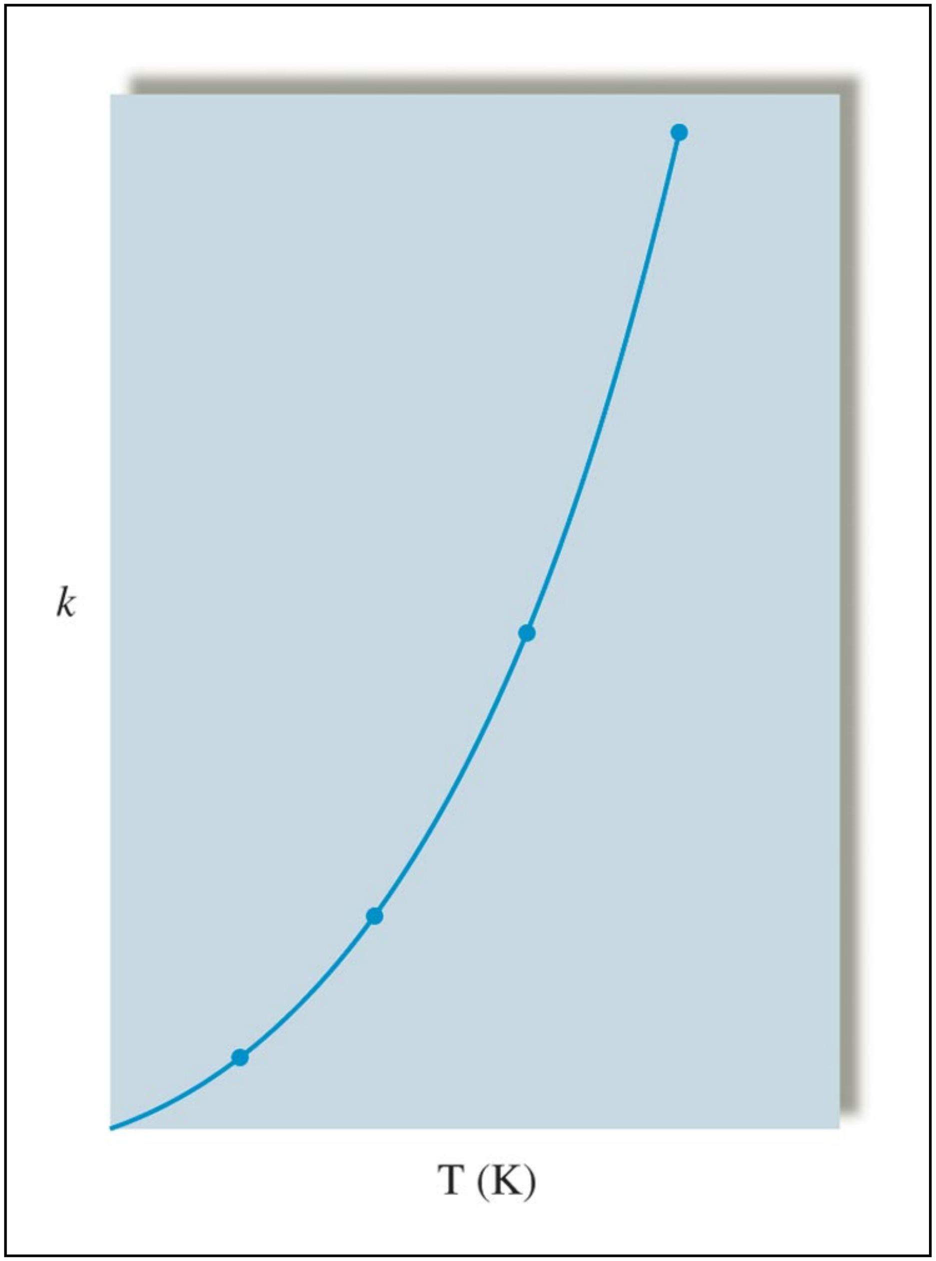


Figure 12.11 a & b (a) The Change in Potential as a Function of Reaction Progress (b) A Molecular Representation of the Reaction

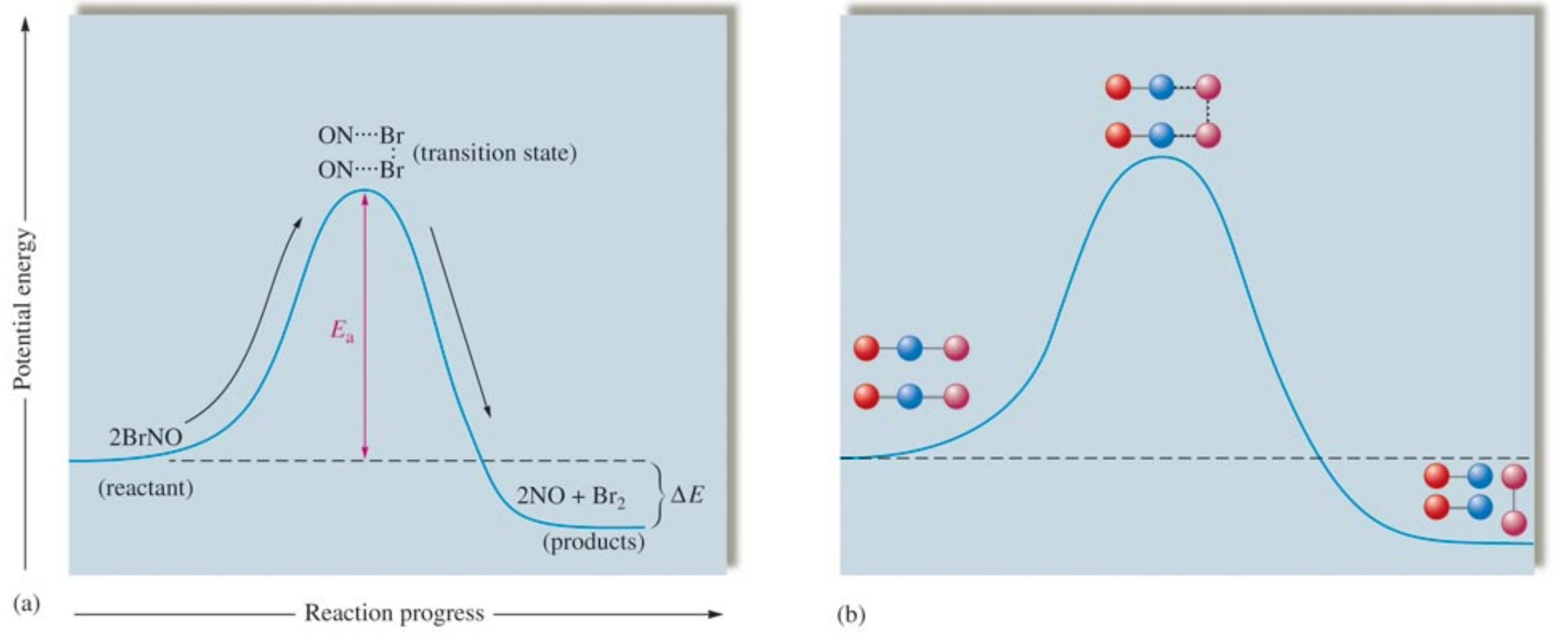


Figure 12.12 Plot Showing the Number of Collisions with a Particular Energy at T_1 and T_2, where $T_2 > T_1$

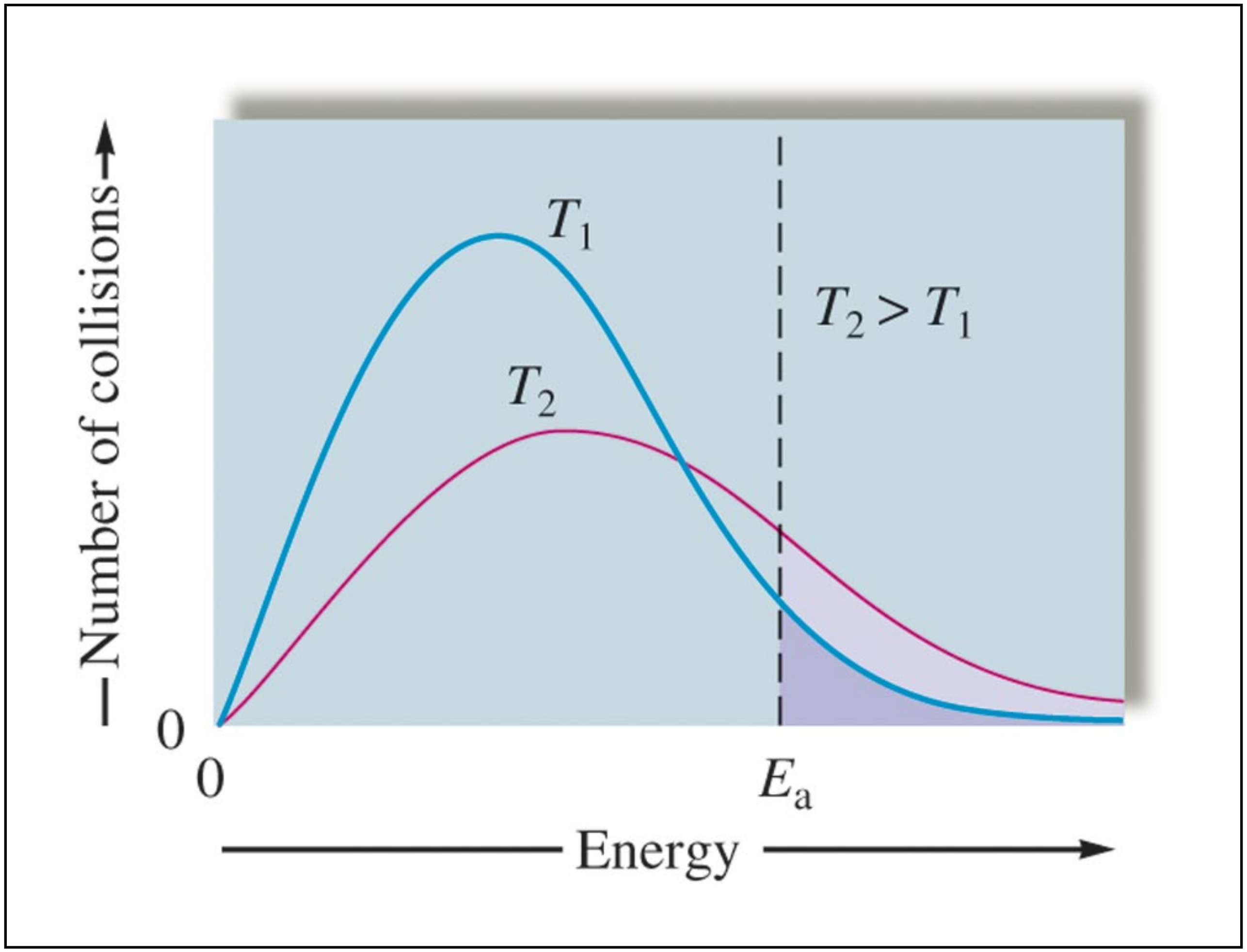


Figure 12.13 Several Possible Orientations for a Collision Between Two BrNO Molecules

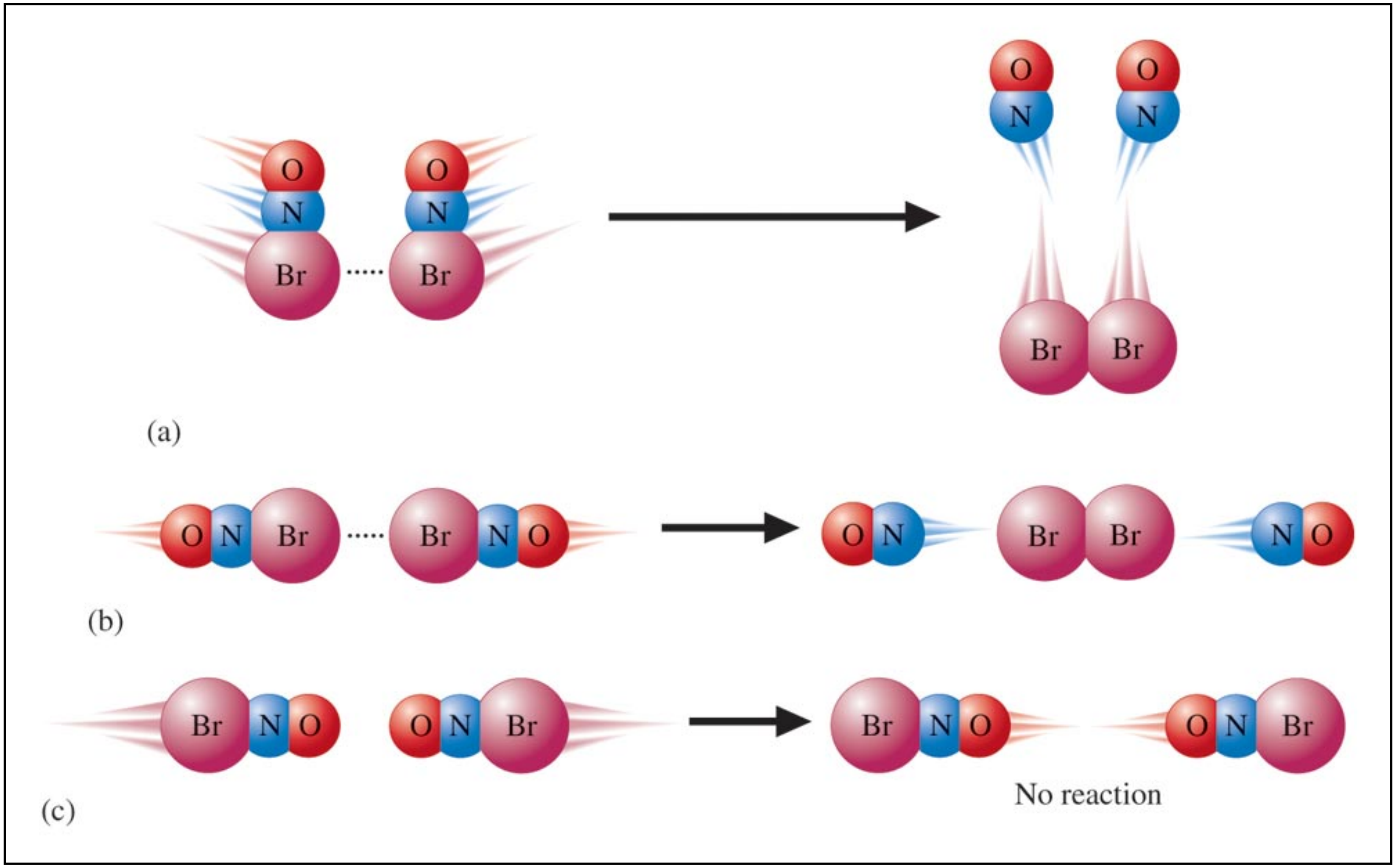


Figure 12.14 Plot of ln(k) versus 1/T for the Reaction of $2N_2O_5$ [illegible] $4NO_2$ (g) + O_2(g)

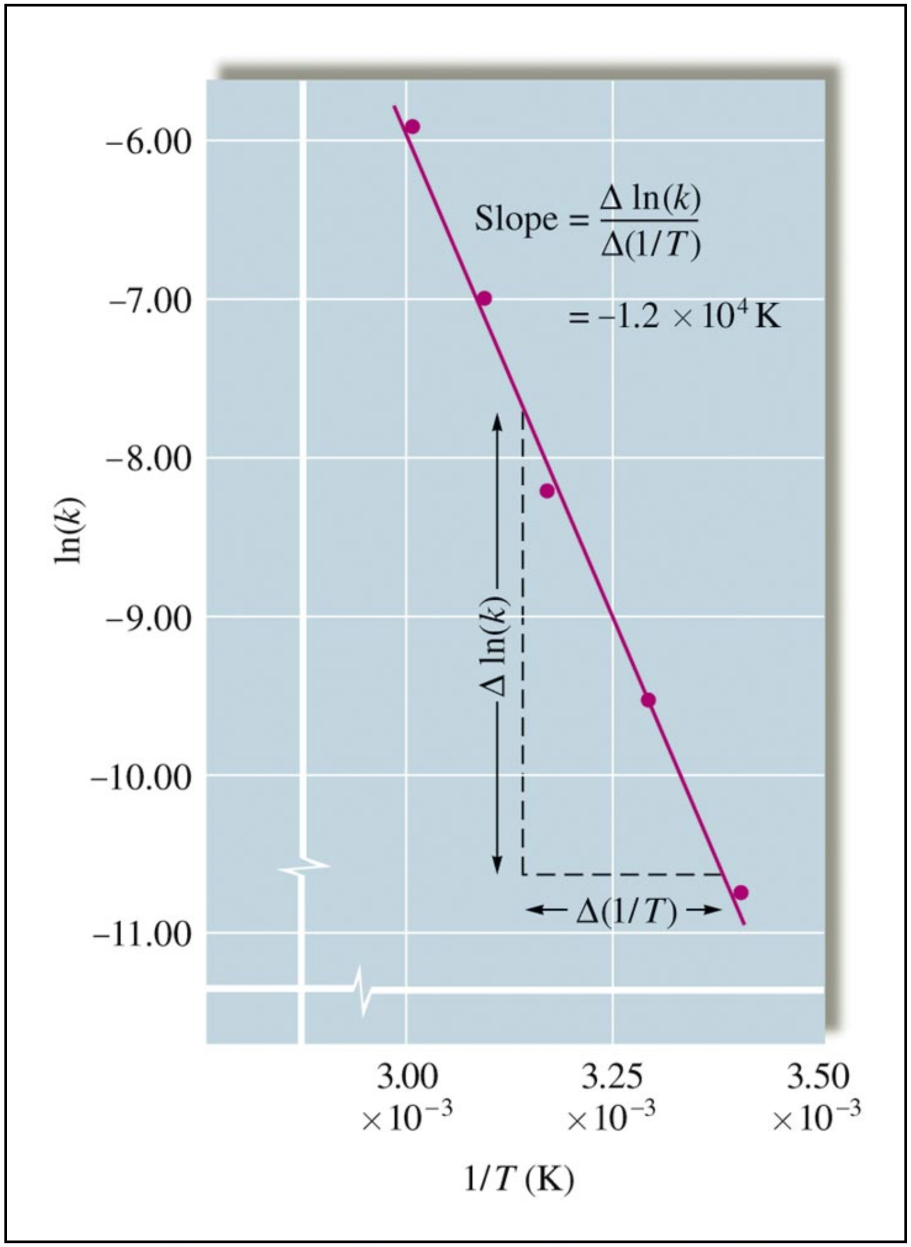


Figure 12.15 Energy Plots for a Given Reaction

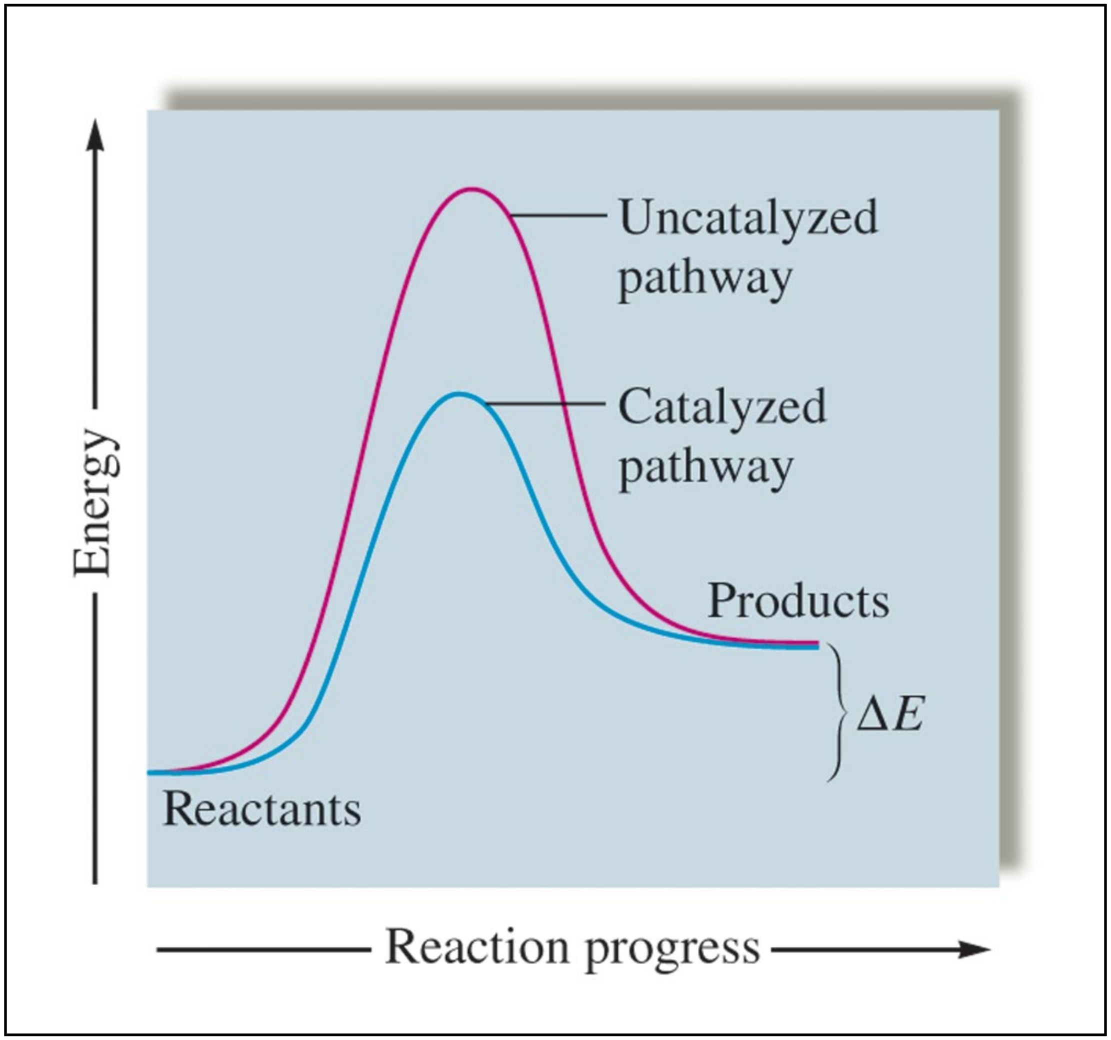


Figure 12.16 a & b Effect of a Catalyst on the Number of Reaction-Producing Collisions

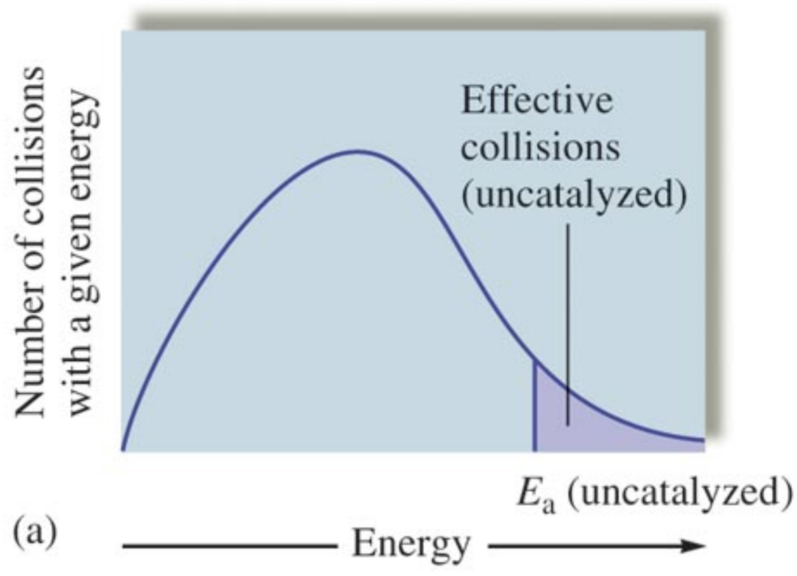


Figure 12.17 a-d Heterogeneous Catalysis of the Hydrogenation of Ethylene

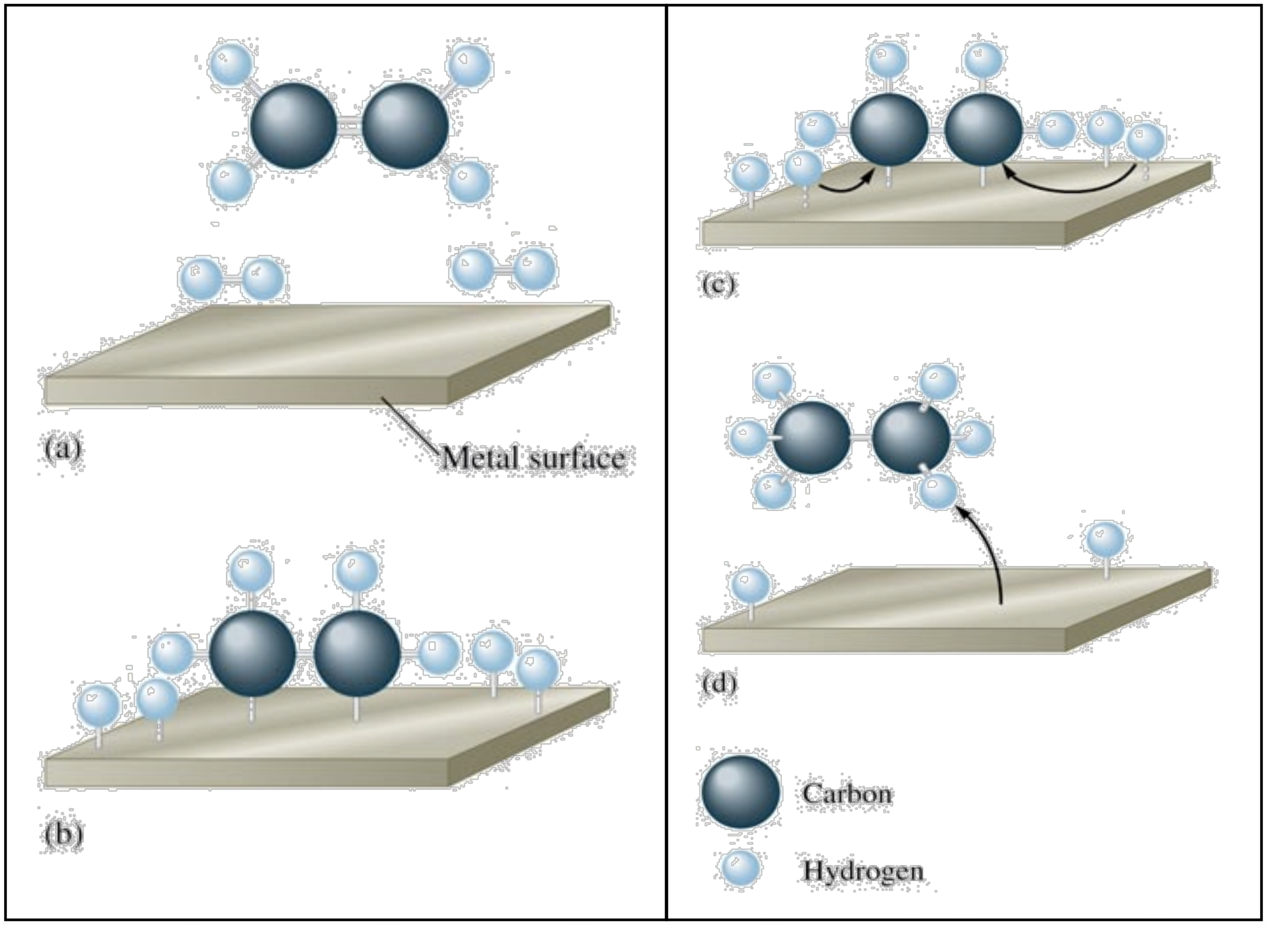


Figure 12.21 Protein-Substrate Interaction